UCA | Universidad de Cádiz

FACULTAD DE CIENCIAS DEL MAR Y AMBIENTALES

PROYECTO DE TESIS DE MASTER DE INVESTIGACIÓN, MASTER EN OCEANOGRAFÍA

Oceanografía

TÍTULO:
DETERMINATION OF ORGANIC MATTER BURIAL RATE IN THE INNER CADIZ BAY: CONTRIBUTION OF DIFERENT HABITATS AND POSSIBLE SOURCES OF ORGANIC MATTER.

Proyecto presentado por

María Jesús Rubio de Inglés

En Puerto Real a 19-20 de abril de 2010

UCA | Universidad de Cádiz

D. Alfonso Corzo, Catedrático del Departamento de Biología (área de ecología) de la Facultad de Ciencias del mar de la Universidad de Cádiz y D. Edward P. Morris, Doctor en biología marina y investigador adjunto de la universidad de Cádiz.

HACEN CONSTAR,

Que el trabajo recogido en la Tesis de Máster, titulada: **"Determination of organic matter burial rate in the inner Cadiz bay: contribution of different habitats and possible sources of organic matter"** presentada por el alumno/a: Maria Jesús Rubio de Inglés, ha sido realizada bajo nuestra dirección.

Considerando que resume su trabajo de investigación y que reúne todos los requisitos legales, autorizamos su presentación y defensa para la obtención del Máster de Oceanografía por la Universidad de Cádiz.

En Puerto Real, a 22 de Noviembre de 2010

Fdo: Alfonso Corzo   Fdo: Edward P. Morris

Abstract

The coastal habitats are important for the global ocean production and provide important ecosystem services. The contribution of coastal ecosystem dominated by macrophytes to the global sequestration and burial of carbon could be important, being the aim of this study to determine the burial rate of C and N of some characteristic habitat from the Cadiz Bay and the sources of the organic matter being buried on long term. The experimental design involved the analysis of key biogeochemical properties, like plant biomass aboveground and belowground, contents of organic matter, C and N, and isotopic fractionation of C and N contents of the sediment, along a transect in the Trocadero Island saltmarshes, from a Zoostera noltii dominated bed (S1) in the low saltmarsh, bare sediment (S2), an area of bare sediment with scattered Spartina maritima plants (S3), to a Spartina maritima dominated sediment in the high saltmarsh (S4). This transect represent a sea to land gradient in marine influence. These four habitats are characteristic of the Cadiz Bay Natural Park and of many other temperate saltmarshes. The horizontal heterogeneity in the biogeochemical characteristics within each habitat was high. The major differences in the biogeochemical characteristics of the sediment were related to the tidal height of each habitat, this is their position in the sea to land gradient. No significant differences were found in the content of organic matter between the different habitats. However, the content in carbonates was significantly lower in the most terrestrial habitat, S3 and S4, than in S1 and S2, being these two habitats more influenced by marine conditions. On the contrary, the organic C and total N content of the sediment tended to increase towards the land. In general, the vertical profiles of the biogeochemical properties did not show a clear trend with depth that might be due to intense mixing of the sediment surface. The analysis of $\delta^{13}C$ and $\delta^{15}N$ and the comparison with previous data suggest that the sediment organic matter seems to have multiple sources, although the organic matter derived from macroalgae and suspended particulate matter represented an important fraction. Our calculation indicates that between 73 - 123 g OM m-2 y-1 are buried in the inner bay, which represents organic C and total N burial rates of between $15.6 – 26.4$ g C m^{-2} y^{-1}, and $2.1 – 3.5$ g N m^{-2} y^{-1}, respectively. Thus, the total annual C and N burial rates for the inner bay, which has an area of 30 km^2, of which the intertidal area is about 13 km^2, are estimated to be about 630 t-C y^{-1} and 84 t-N y^{-1}.
Key words: burial rate, salt marsh, sediment biogeochemistry, Cadiz bay.

Resumen.

Los ecosistemas costeros son importantes para la producción oceánica global y generan servicios al ecosistema. La contribución de los ecosistemas costeros dominados por macrófitos en la captura y enterramiento del carbono pueden ser importantes y esto dio lugar a los objetivos del presente estudio, en el cuál se determina el enterramiento de C y N en los hábitats característicos de la zona y las fuentes de materia orgánica que pueden llegar a ser enterradas durante un largo periodo de tiempo. El diseño experimental incluyó el análisis de las propiedades biogeoquímicas más importantes para esta determinación, estas fueron la biomasa de las plantas (raíces y tallos), contenidos de materia orgánica, C y N y por último la fraccionación isotópica de los contenidos de C y N del sedimento; esto se llevo a cabo a lo largo de un transecto linear en la marismas de la isla del Trocadero, desde el lecho dominado por Zostera noltii en la marisma baja (S1), el sedimento desnudo (S2), sedimento desnudo donde la Spartina maritima empieza a aparecer (S3) y el lecho dominado por Spartina maritima (S4) en la marisma alta. Este transecto representa un gradiente de influencia marina desde el mar hasta tierra. Estos hábitats son característicos del parque natural de la bahía de Cádiz y de otras marismas de climas templados. Se encontró una elevada heterogeneidad en las características biogeoquímicas de cada hábitat. Las mayores diferencias biogeoquímicas del sedimento se debieron a la posición de cada hábitat en el gradiente mar-tierra y por tanto a la altura de marea. No se encontraron diferencias significativas en las concentraciones de materia orgánica sin embargo, los carbonatos fueron menores para las zonas más alejadas del mar. Por el contrario el contenido de C y N aumento en los puntos más cercanos a tierra. Los perfiles verticales no mostraron ninguna clara tendencia, quizás debido a la intensa mezcla en la superficie del sedimento. Los análisis de $\delta^{13}C$ y $\delta^{15}N$ y la comparación con datos de otros estudios, mostraron que la materia orgánica en el sedimento provenía de varias fuentes aunque las macroalgas y la materia particulada suspendida tienen una especial relevancia. Los cálculos realizados indican que entre 73-123 gOM m^{-2} año^{-1} son enterrados en la bahía interna, lo cuál representa un enterramiento de C entre 15.6-26.4 gC m^{-2} año^{-1} y de N entre 2.1-3.5 g N m^{-2} año^{-1}. Por lo tanto la velocidad de enterramiento de C y N en la bahía interna con un área de 30 km^2 y en el intermareal con un área de 13 km^2 es de 630 t-C año-1 y 84 t-N año-1.

Palabras clave: Velocidad de enterramiento, marisma, biogeoquímica del sedimento, Bahía de Cádiz

INDEX

INTRODUCTION

1.1 The value of coastal ecosystems

Coastal ecosystems are among the most productive in the world (Nellemann et al., 2010). They support approximately 20% of the total primary production of the oceans. This high productivity is because they have an elevated supply of nutrients from coastal upwelling, river inputs, human activities (Nielsen et al., 2004) and underground water (Niencheski et al., 2007). Because of the important ecosystem services they provide, they make an important contribution to the total welfare of the planet. Indeed, scientists have attempted to assess the value of coastal ecosystems in terms of economics, and suggest that they provide services with an annual value close to 33 trillion dollars (Costanza et al., 1997). Even considering the huge uncertainties involved in this type of study, it is clear that the services provided by coastal ecosystems are very important and that destruction of these habitats has implications for human welfare (Costanza et al., 1997). Recently the capacity of coastal ecosystems dominated by marine macrophytes to sequester and bury carbon has been highlighted as one the particularly important ecosystem services that these habitats provide (Nellemann et al. 2010). Hence, the general purpose of this study is to analyse whether this hypothesis is supported in Cadiz Bay, which contains large extensions of seagrasses and saltmarshes.

1.2 Carbon sequestration and burial in vegetated coastal habitats

Vegetated coastal areas can act as a carbon sink (Wang and Cai., 2004; Sousa et al., 2010) (i.e., remove greenhouse gases from the atmosphere IPCC AR4, 2007). Coastal shallow habitats rank amongst the most productive areas in the world, comparable with agricultural crops and tropical rain forest (Whittaker 1975, Duarte and Cebrian 1996). These habitats are able to fix CO_2 into organic matter using photosynthesis. The majority of this production is grazed by animals, degraded or exported to adjacent ecosystems. However, a small amount remains available for accumulation within the system. Generally, the detritus produced by different primary producers has different degrees of biodegradability (Rice et al., 1981, Enriquez et al 1993) and can be highly refractory to microbial degradation. For example the accumulation of refractory organic carbon is 4 fold higher for higher plants (10-17 % of

net primary production) than for algae (0.4-6 % of gross primary production, Duarte and Cebrian 1996, Cebrian 2002).

Also the large amounts of below-ground (BG) biomass of many macrophytes favours the direct accumulation of organic material in sediments. The majority of halophytes have a greater contribution (> 50 %) of below-ground material to the total biomass production (Sousa et al., 2010). Several authors have pointed out stressed conditions affect biomass production (Ibañez et al., 1999, 2000) by reducing above-ground (AG) biomass and inducing plants to invest in below-ground material (Edwards et al., 2005), although the opposite is often observed for seagrasses. Salt marsh age also affects AG/BG biomass ratios and total production (Valiela et al., 2000, Sousa et al., 2008).

Furthermore, in many cases the origin of a significant part of the organic matter in the sediments of vegetated habitats comes from plankton (Garcia et al., 2002) and detritus i.e., it is imported as suspended particulate matter. Indeed, a great number of macrophyte habitats are considered to act as a "nutrient buffer" between terrestrial and coastal systems (Sousa et al., 2008; Lillebo et al., 2004; Sousa et al., 2010).This can be attributed to the effect of macrophytes on hydrodynamics; tending to reduce current velocities at the sediment surface and favour particle trapping (Hendriks et al., 2008). However, protection of the bed from high current velocities and wave energy (Peralta et al. 2008) and thus prevention of resuspension maybe a more important mechanism by which vegetated habitats increase long-term sediment accretion rates. This is because long-term accretion rates are the balance of surface deposition and erosion and thus represent the net accumulation of sediment at sufficient depth below the surface (Nielsen et al., 2004).

Burial of organic matter is defined as the permanent transfer of material from the active layer (influenced by hydrodynamic and biological processes) to deeper layers. Thus, OM burial rates can be calculating using the sediment porosity (Φ), accumulation rate (ω, cm y^{-1}), dry density of particles (ρ) and the OM content below the active layer (C_i) (Nielsen et al., 2004):

$$Burial = (1-\Phi) \cdot C_i \cdot \rho \cdot \omega$$

By using the OM content and accumulation rate below the active layer, material that is lost via mineralisation and export is not included in estimates of burial. However, this does mean that sediment cores must be deep enough to define the active layer and that accumulation rates are required, which are generally measured using radionucliotides (Ligero et al. 2002, Nielsen et al., 2004). Fortunately, sediment accumulation rates have been measured in Cadiz Bay and are between 0.16 and 0.27 cm y^{-1} (Ligero et al. 2002).

Much of the controversy about global estimates of C burial by vegetated coastal habitats centres around the use of surface deposition rates and OM contents for burial estimates and essentially neglecting export and mineralisation. For example, globally, vegetated coastal habitats are estimated to have a burial rate of 120–329 Tg C y^{-1}, which accounts for at least half of the lower estimate of global carbon burial in marine sediments. However, other studies have estimated that estuaries, salt mashes and mangroves emit to the atmosphere up to 500 TgC·y^{-1}·(Cheng-Tung et al., 2009). Thus, there still remains some uncertainty about OM sediment fluxes, export and mineralisation in shallow coastal habitats.

1.3 Organic matter sources

Indications about the sources of OM can be derived by using tissue biomarkers that can help separate between different primary producers. The elemental analysis of C:N ratios has been used to distinguish algal and land-plant organic matter origins. Whereas algae have C:N ratios between 6.6 and 10, land plants ratio is around 20 (Meyers, 1994). This distinction is created by the lack of cellulose in algae and the great amount in terrestrial plants and the high amount of organic matter in algae. The protein compounds in algae and plants can decrease when degraded and raise C:N ratios (Craft et al., 1988).

Carbon and nitrogen stable isotopic composition can also be used to determine the precedence of the organic matter found in the sediment. Although, $\delta^{15}N$ values tend to be similar for all primary producers growing on the same N source they can give useful information about terrestrial sources (Morris et al. 2009). However, for $\delta^{13}C$, depending on the photosynthetic pathway ^{13}C fractionation is different. The majority of plants use C3 photosynthesis to assimilate organic matter, and the

fractionation of $\delta^{13}C$ is around -20 ‰, plants which use C4 Hatch-Slack photosynthesis create a diffusional isotope shift of -7 ‰ (Raven et al., 1995). When atmospheric CO_2 ($\delta^{13}C \approx$ -7 ‰) is used by C3 plants their tissues have an average $\delta^{13}C$ value of more or less -27 ‰ and for C4 plants it is around -14 ‰. Algae and the C3 plants inside the water may use dissolved CO_2, which usually is in isotopic equilibrium with the atmosphere or dissolved bicarbonate, which has $\delta^{13}C$ value of around 0 ‰ (Meyers, 1994, Raven et al., 1995).

1.4 Aims

The Cadiz Bay contains a variety of vegetate and unvegetated habitats and organic matter sources. These habitats, dominated by characteristics plant species, are distributed according to a zonation pattern with characteristics tidal height, in a sea to land gradient depending of their relative resistance to the immersion and emersion stress.

The present study aims to examine the burial of organic matter within sediments of different intertidal habitats. We hypothesise that because of the benthic macrophyte communities, different rates and pathways of organic matter burial will be found in intertidal sediments of Cadiz Bay. These differences should be apparent as modifications of sediment organic matter profiles and stable isotopes of carbon and nitrogen ($\delta13C$ and $\delta15N$). Thus, the aims of this study are:

- Examine differences in sediment properties between intertidal habitats of *Z. noltii*, bare sediment and *S. maritima*.

- Attempt to infer the most important organic matter sources in each habitat via stable isotope analyses.

- Try to up-scale this information in combination with previous studies to estimate organic matter burial of intertidal habitats within Cadiz Inner Bay.

MATERIAL AND METHODS

2.1 STUDY SITE

This study has been carried out in Cadiz Bay. The samples have been taken at Trocadero Island (SW Spain; 36°23′–36°37′N and 6°09′–6°21′W, Natural Park). This area was declared natural park on July 1989 and it is a special place for the bird migration between Europe and Africa. The bay situation is between Doñana's national park and Gibraltar Strait (Figure 1) (Paneque P. et al, 2007).
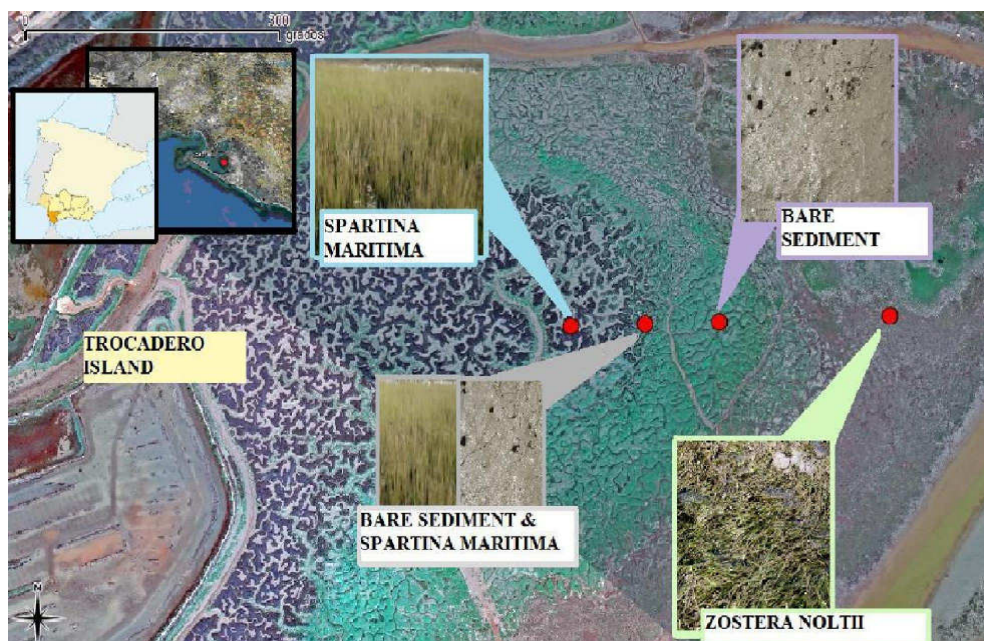

Fig 1 : Study area and different sampled points. Here is showed the area inside Spain, inside the bay and Trocadero

Cadiz, Chiclana, Puerto de Santa Maria, Puerto Real and San Fernando surround the natural park and discharge wastewaters in different degree to the inner Cadiz Bay (figure 2). At the south west is placed the Atlantic Ocean and at the north east the bay. Around 400.000 people live surrounding this natural park.
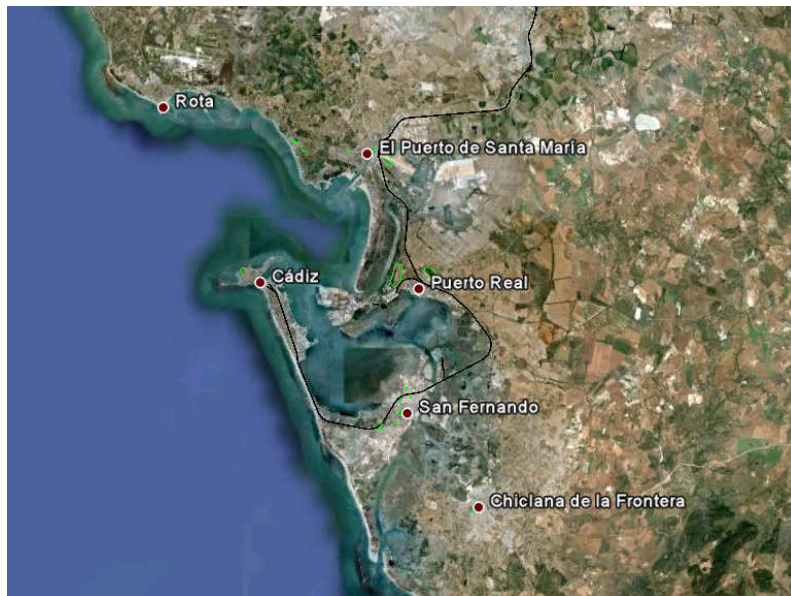
Fig 2: Cities surrounding the nacional park.

The Bay climate is Oceanic-Mediterranean. The temperatures are around 17ºC during all the year and the dominant wind is usually from the East. The rainfall average is about 600 mm/year and the Cadiz bay receive 3000 of sun hours per year. The evaporation is greater than the rainfall. The direction of the wind affects to the humidity of this area. The wind coming from the east (Called Levante) is dry and the one coming from the west (called Poniente) is wet (PORN, Cádiz).

The Cadiz Bay can be divided in two different areas, the outer and the inner bay. The outer bay is linked to the open ocean and has more oceanic characteristics, being well exposed to the waves, winds and tides. The inner bay is characterized by shallow waters and the most important pressure is the tides action. One of the most characteristic features of the inner bay is the large extension of tidal flats. The areas affected by tides can support several seagrasses species like *Zoostera Noltii, Zostera marina* and *Cymodocea nodosa*. Those ones have an important role at these coastal sites. The high part of the marsh is most unstable and *Spartina maritima* was the first plant which could colonize this habitat. The *Salicornia sp*. followed this colonization creating a new ecosystem very typical at the research site. The different vegetated an unvegetated

habitats are organised in a characteristic zonation pattern depending on their resistance to emersion and immersion stresses by the semidiurnal tides.

Few decades ago large extensions of the area were covered by salt marshes, however nowadays only three large and well preserved areas can be found: Toruños salt marsh (El Puerto de Santa María), Trocadero and inner bay salt marshes (Puerto Real) and the Sancti Petri salt marsh (Chiclana de la Frontera).

2.2 SAMPLING DESING

The samples were taken in Cadiz Bay (SW Spain; 36°23′–36°37′N and 6°09′–6°21′W, Natural Park). Sampling method was carried out by a linear transect along the salt marshes and intertidal zone (Trocadero Island). This wetland is dominated by herbs, grasses and low shrubs (Adam P., 1990). The most important characteristic is the distinct vegetation zones along a gradient of frequency and duration of tidal inundation. Three sampling areas were chosen: Sediment dominated by *Zostera Noltii* (S1), bare sediment (S2), bare sediment affected by *Spartina maritima* (S3) and *Spartina maritima* meadow (S4).
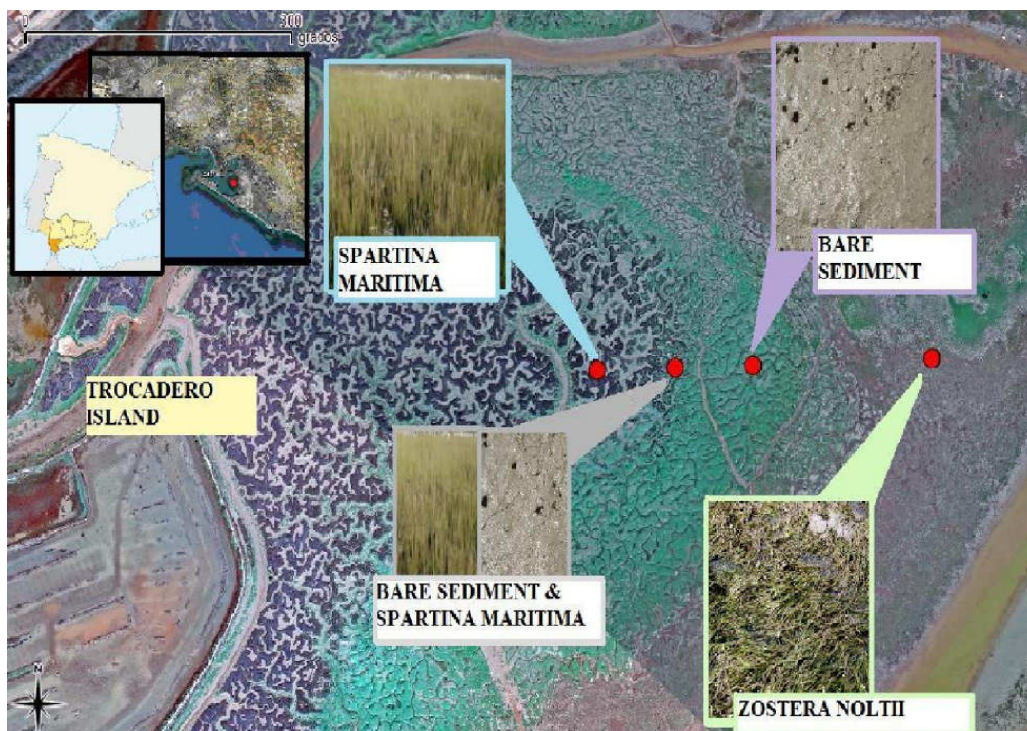

Fig 3: Sampling site (Trocadero Island, Inner bay) and linear transect. Source: Landsat

The sample site was reached by boat (figure 4). Then, the samples were taken by cores of 1 meter large but the sediment just reach around 60 cm depending on the compactness of every site (figure 5), Once the cores were taken, biomass from plants was collected from *Z. Nolti* and *S. maritima* using a box core. The samples set was composed by 3 replicates from 4 different areas, a total of 12 cores of 1 meter high and 4 plastic cubes (2 for above ground and 2 below ground) with the material collected with the box cores (those samples were collected from *S. maritima* and *Z. Nolti*). All samples were taken to the laboratory where plant material was rinsed several time to cleaned from mud, stored plastic bags, labelled and kept at -20ºC. The cores were also cleaned around with water and were kept inside the freezer at -20ºC.

Fig 4: Material carried by boat to the sampling site.

Fig 5: Cores used on sampling 1 m large

2.3 SAMPLE PREPARATION

Sediment samples

The cores were cut in 2 centimetre slices, kept, weighted, dried and grinded (figure 6 and 7). The water content is calculated by the difference between fresh and dry weight.. Then the organic matter and the carbonates were analyzed.

Fig 6: Set of samples 288 sediment samples.

Fig 7: Cutting the cores

Plant material

Macrophytes were cleaned of mud and epiphytic material. Algae were removed from seagrasses and were kept for identification (figure 8). After cleaning, biomass was stored at -20 ºC The plants were weighted after defrost them, afterwards were dried to

loss the water content and weighted again (figure 9). A small part of the biomass was grinded and sent to analyse the isotopic content.

Fig 8: Spartina maritima cleaned from mud and algae. Two box cores from above and underground were taken.

Fig 9:   Weighting biomass.

Biomass from sediment cores

The roots biomass from the first centimetres in *Zoostera Noltii* and *Spartina maritima* areas were removed from the sediment and were treated like the plants biomass mentioned before (figure 10). The fresh sediment was weighted before remove the roots from there, then treated like the rest of samples and finally, the roots were frozen. The roots, in other hand, were first weighted after defrost, second grinded and third were ready to send. Only two profiles were selected and sent to analyze the isotopes. The roots were separated by rinsing the sediment with distilled water. This sediment was kept in the oven at 60 ºC until the water content disappeared.

Fig 10: Separation of roots biomass from each core slice.

2.4 SAMPLES ANALYSIS

Water content, porosity, dry weight and fresh weight

The water content was analysed at different depths. The used parameters were the fresh and dried weight. The fresh was measured immediately after cut the core and the second parameter was measured after dried the sample using an oven at 60ºC aprox. during 4 or 5 days.

The determination of the water content was calculated as:

$$Wa = \frac{WW - DW_{105}}{WW} \cdot 100$$

Where:

Wa (%) = Absolute water content (%)

WW (g) = Fresh weight (grams)

DW (g) = Dry weight (grams)

The procedure for the porosity was the same as used for the water content above but the determination was different.

$$P = \frac{WW - DW_{105}}{h \cdot r^2 \cdot \pi}$$

Where:

DW_{105} (g)= Dry weight (grams)

WW= Fresh weight (grams)

h= height (centimetres)

r= radius (centimetres)

Using the same parameters (fresh and dried weight) dry and wet density could be calculated.

Dry density followed the next equation:

$$\delta_{dry} = \frac{DW_{105}}{h \cdot r^2 \cdot \pi}$$

Where:

DW_{105} (g) = Dry weight (grams)

h= height (centimetres)

r= radius (centimetres)

And the wet density is calculated by:

$$\delta_{wet} = \frac{WW}{h \cdot r^2 \cdot \pi}$$

Where:

WW= Fresh weight (grams)

h= height (centimetres)

r= radius (centimetres)

Organic matter

The organic matter content was calculated as loss weight on ignition (LOI) according to Nelson et al 1996 (modified). The burnt weight is obtained after calcination in a muffle furnace during 5 hours at 550ºC (Sutherland 1988).

The samples were removed from the muffle and were stored inside the oven for a while. Then, to avoid the dampness the sample is kept at the desiccator. When the sample colds down is weighted and kept again in the oven with 1 mL of distilled water. This water was added because the bay sediment has high clay content and the clays have to rehydrate to give the correct loss weight on ignition (modif. Nelson et al, 1996). Once the water disappears, was weighted again and this weight was used for the organic matter determination.

The determination of the organic matter content was calculated as:

$$OM = \frac{DW_{105} - BW_{550}}{DW_{105}} \cdot 100$$

Where:

OM= Organic matter content (%)

DW= Dry weight (grams)

BW= Burnt weight (after the addition of distilled water) (grams)

Carbonates

A gram of sediment was measured and put inside a plastic bottle. After this measure a tube which contents Hydrochloric acid was added and the bottle was hermetically closed. After that, a needle was put at the top to equilibrate the bottle with the environmental atmosphere pressure. Ten minutes later, the needle was removed and the Hydrochloric acid was mixed with the sample. Half an hour later the pressure inside the sample is measured with the differences in the Hg column before and after prick the sample with a needle connected to the column (Balázs et al., 2004)

Knowing the elevation of the column using a blank and a sample of carbonates with one known weight the calibration could be done and the samples could be analyzed.

This method is used by several researches and is know wide world.

Stable Isotopes

The stable isotopes were separated in two different sets. One set was prepared for isotopic analyses and the second did not have any treatment before being sent. The treatment used was the acidification or not acidification of the sample. The acid was added to remove all the inorganic carbon from the sample.

The one prepared to analyse the isotopes was stored in crucibles inside the oven and regularly 1 ml of hydrochloric acid was added until the effervescence stops. Once the complete process was done the samples were kept in eppendorf and sent to Iso-Analytical Limited Company in Cheshire (UK).

The heavy and light isotopes are compared using the δ expression. With this system a negative number shows a depletion and a positive number shows an enrichment, standards are C from Pee Dee Belemnite and N from the air (Machas et al.; 2003). The relation was done by the next equation:

$$\delta^{13}C = (\frac{^{12}C/^{12}C_{sample}}{^{13}C/^{12}C_{s\tan dard}}) \cdot 10^3$$

2.5 STATISTICS

Calculations having into account the porosity

All values in percentage were changed into g·m3. This change was mainly realized because we were checking the amount of the wished variable on sediment, but we did not analyse the aqueous phase. Then, having into account the porosity the change of units was done.

$$Variable(g/m3) = Variable(\%) \frac{DW}{2 \cdot r^2 \cdot \pi}$$

Where:

Variable (g/m^3) was the units we want.

Variable (%) was the variable units we had.

DW was the dry weight

r was the ratio

ANOVA

We observed not important variation at the firsts 22 cm. Then an ANOVA was realized to check differences between profiles. The profiles were evaluated just taking this 22 cm, that acted as a surface and then the depth was taken as a factor. The software used was R.

Box plots

Box plots were done at this 22 cm. Those plots showed graphically the differences found with the Nested ANOVA test. The box showed the media, the box was 25 and 75% quartiles, the whisker was the factor range and the points were the outliers. The software used was R.

Trend with depth

All profiles were analysed to show to trend with depth they had. To make this possible, each area was fit with an exponential equation.

$$C_z = C_0 e^{-k \cdot z}$$

Where:

C_0 was the concentration at the inicial depth.

The coefficient k, is the specific rate of change with depth, having positive or negative values depending whether the variable increases or decreases with depth.

z was depth

C_z was the concentration or value of the variable at depth z.

After applied this equation, one line was fitted at each profile to show it graphically. Non-linear least squares were used to fit the equation, the p-value was shown at all profiles and significant differences were one p-value lower than 0.05, and the 95 % CI coefficient was also given. The software used was R.

$\delta^{13}C$ and $\delta^{15}N$ plots

To plot $\delta^{13}C$ against $\delta^{15}N$ for our data the error standard was used to have more confidence with results.

$$Error(std) = \frac{Std}{\sqrt{N}}$$

Where:

Std was the standard deviation.

N was the number of samples.

The software used in that case was Microsoft excel.

The bag plots are graph which showed the media at the central point, the 75 % of data with dark colour and the rest of data with light colour. Those graphs have been used to show the different sources around the bay. The software is was R.

Burial rate

To calculate the burial rate the deepest values for organic matter, carbon and nitrogen where selected. Then with these values the media was calculated.

$$X = \frac{\sum N1, N2, N3...Nn}{N}$$

X was the media

N1, N2, N3 were the values of each sample

N was the total number of samples.

The next step was the application of an equation for burial (Soren et al., 2004).

$$Burial = (1 - \Phi) \cdot C_i \cdot \rho \cdot \omega$$

Where:

Φ = porosity

Ci = deep concentration

ρ = dry density

ω = accumulation rate.

The software used was Microsoft excel.

RESULTS

3.1 Plant biomass

Spartina maritima and *Zostera noltii* presented similar aboveground biomass. However there were important differences in their belowground biomass, the amount of *S. maritima* (3.84 kg·m^{-3}) almost triplicates the amount of *Z. noltii* (1.32 kg·m^{-3} g). The Above-Below ground ratio for *Z. noltii* wet was 0.87 and for *S. maritima* 0.26.

However the results are different when analysed in terms of dry weight (Fig. 11). The underground biomass of both plants was similar but *S. maritime* (0.54 kg·m^{-3}) reached a higher biomass than *Z. noltii* (0.4 kg·m^{-3}). The above-under ground ratio for dried *Z. noltii* was 1.2 and the same for *S. maritima* was 0.31.
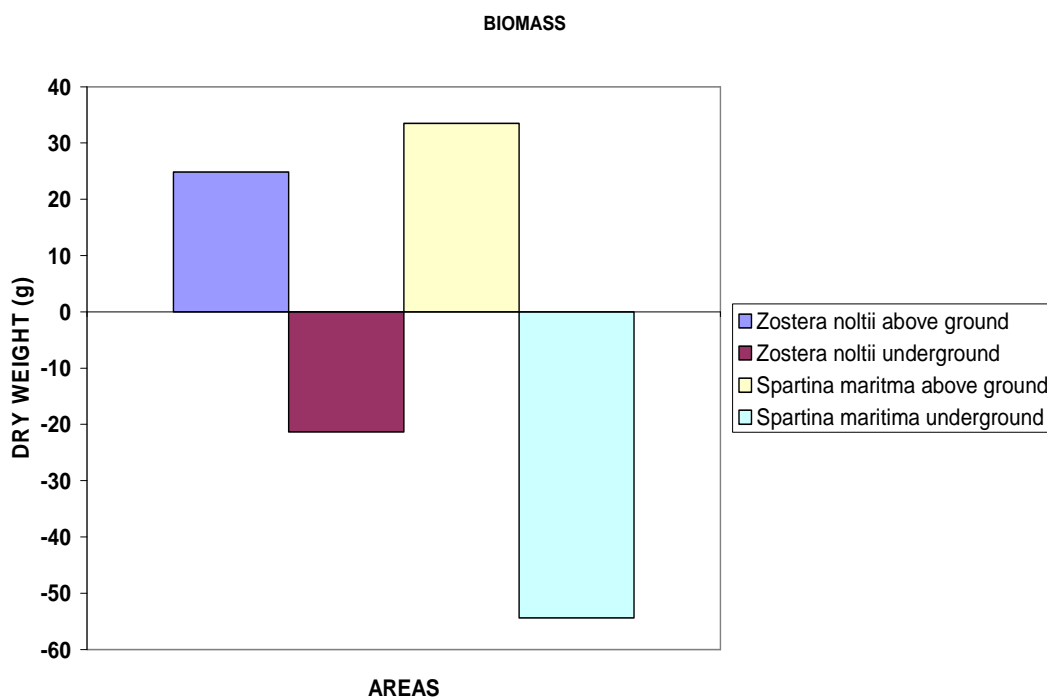
Fig 11: Biomass of *S.maritima* and *Z.noltii* under and above ground took with a box core.

The underground biomass decreased in both communities with depth (Fig. 12) Roots were absent below a depth of about 17 cm in both cases.

ROOTS VS DEPTH
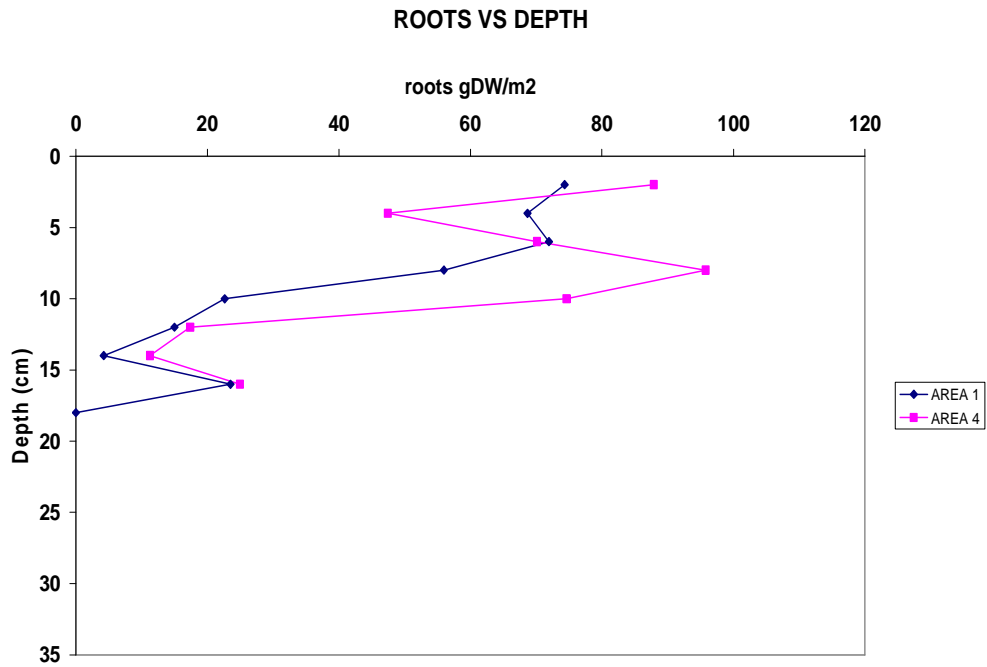
Fig 12: Roots profiles of Z.noltii (Area 1) and S.maritima (Area 2)

3.2 Organic matter and porosity

The organic matter content of the sediment is presented in two ways, 1) as percentage of sediment dry weight (Fig. 13B), and 2) as weight per volume (13C), therefore taking into account the differences in porosity (Fig. 13A). Porosity ranged from 0.4 to 0.8. Organic matter ranged from 6 to 16 % or 10 to 36 for kg.m^{-3}. Porosity and OM did not change significantly with depth in any area. The existence of possible differences between areas in surface (0 - 22 cm) sediment porosity or OM was tested using nested Nested ANOVA. Porosity was significantly different between areas (ANOVA, $F_{3.44}$ = 6.5; p < 0.001), however the grouping of means was not very clear (Fig.14A, Tukey HSD test, p < 0.05). Bare areas (S2 and S3) had a higher water content (higher porosity) than their respective adjacent habitats (S1 and S4), although the vegetated habitats were not significantly different. In contrast, sediment organic matter did not change significantly between areas, either expressed as percentage or as kg.m^{-3} (Fig. 14 B and C).
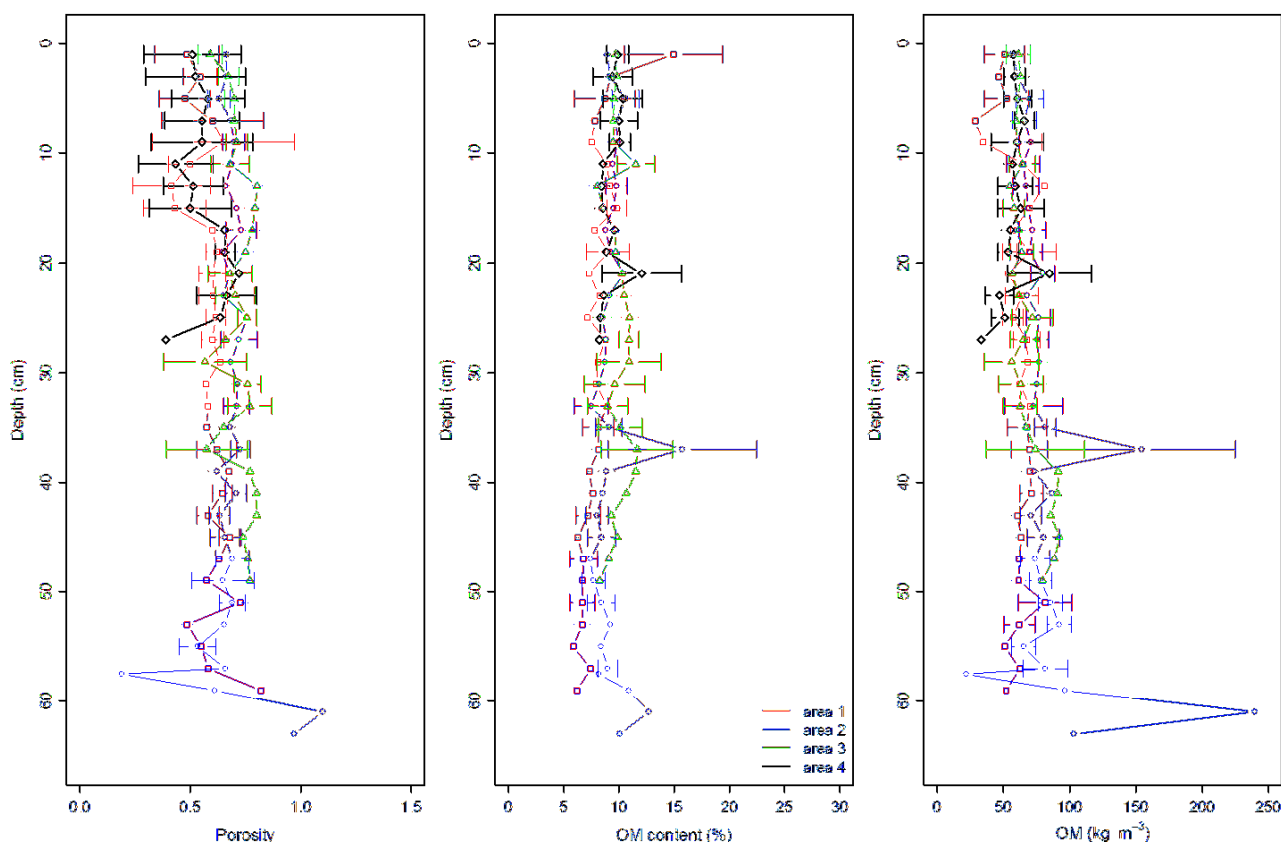

Figure 13. Depth profiles (mean ± SE, n = 2-3) of porosity (A), OM content (B) and OM concentration (C) in each area (1-4 represents *Z. noltii*, bare sediment, bare sediment-SM and *S. maritima*, respectively).
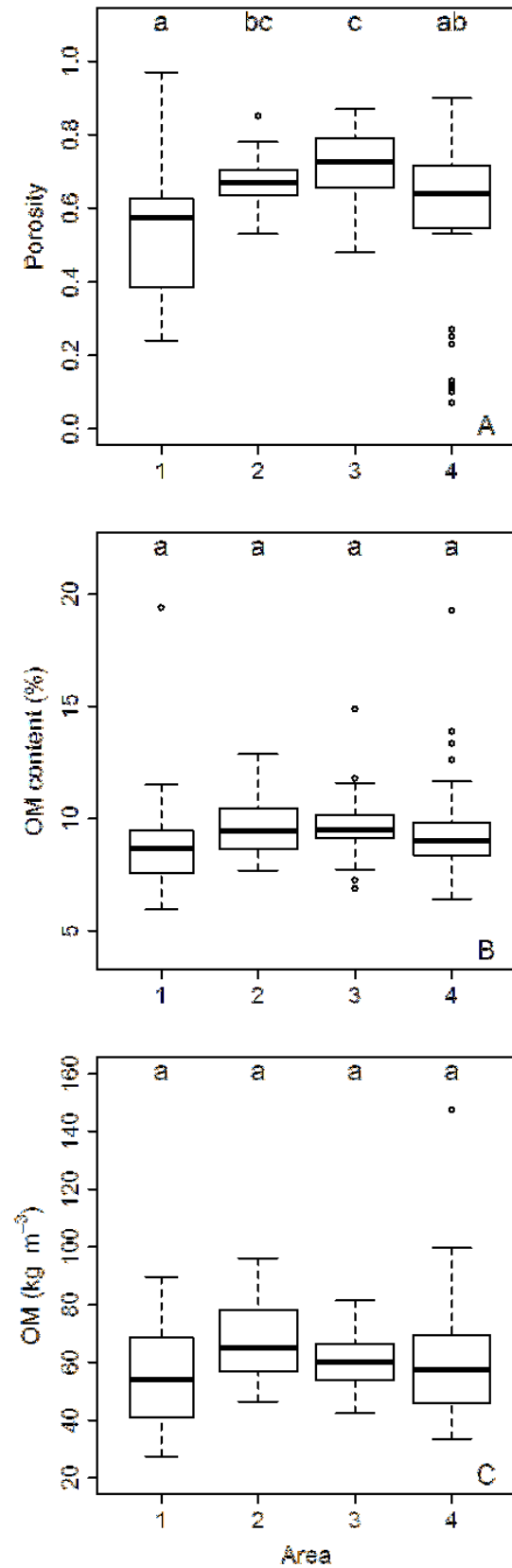
Figure 14. Boxplots of surface (0 -22 cm) sediment porosity (A), OM content (B) and OM concentration (C) in each area. Details as in Fig. 13.

3.3 Carbonate content

The carbonates ranged from 10 to 120 Kg·m⁻³ (Fig. 15). The statistics showed significant differences between different areas (ANOVA, $F_{3.18}$ = 25.7; $p < 0.001$). Carbonate content in area 1 and 2, closer to the sea, were significantly higher than in areas 3 and 4 (Tukey HSD, $p < 0.05$). The carbonate content increased significantly with depth in the areas 1 (k = -0.02, $p < 0.001$) and 2 (k = -0.01, $p < 0.001$), but changes with depth were not significant for area 3 (k = -0.02, $p = 0.15$) and 4 (k = 0.005, p < 0.6).
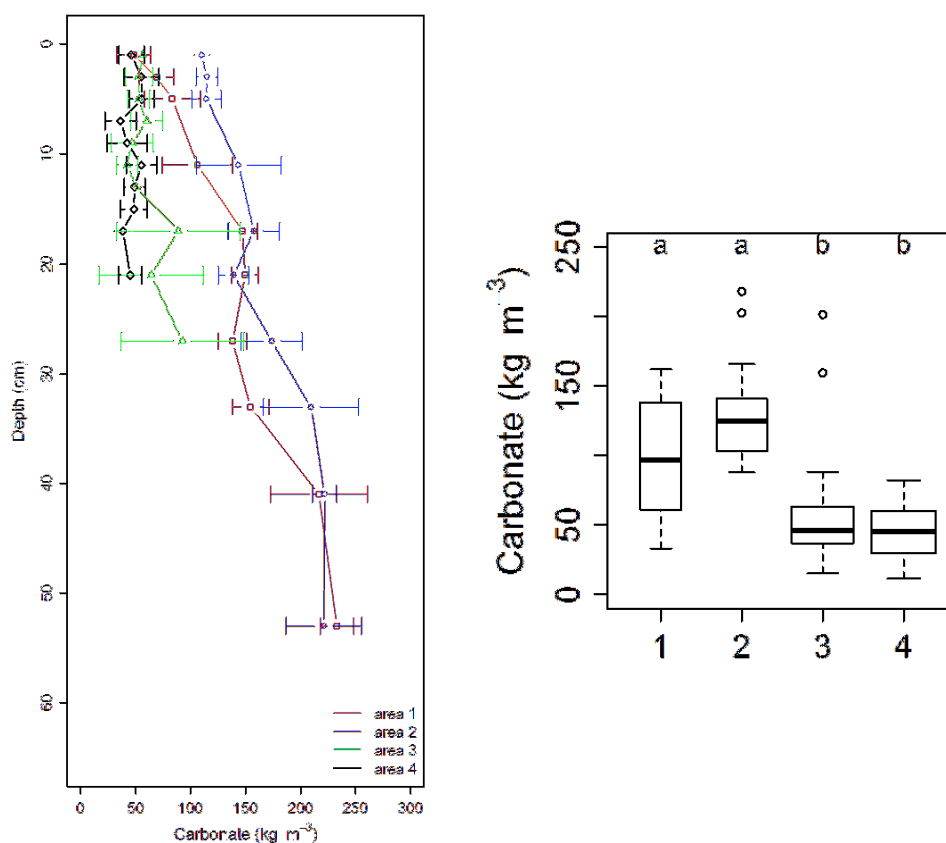
Figure 15. Depth profiles and mean surface sediment carbonate concentration. Details as in Fig. 13.

Organic Carbon and N content

The organic carbon ranged from 1.8 to 5.1 Kg·m^{-3} (Fig. 16A) and was significantly different between areas (Nested ANOVA, F$_{3.27}$ = 23.61; p < 0.01). The carbon content in the areas 3 and 4 was significantly higher than in area 1 (Fig. 17A, Tukey HSD, p < 0.05). No significant trend was observed in the changes of C with depth. Nitrogen ranged from 0.28 to 0.79 kg·m^{-3} (Fig. 16B) and was also significantly different between areas (ANOVA, F$_{3.27}$ = 6.1; p < 0.01). As for C, N content in the areas 3 and 4 was significantly higher from those in the area 1 (Fig. 17B, Tukey HSD, p < 0.05). In general, N tended to decrease with depth, but this decrease was only significant in the case of area 3 (k = 0.009, p < 0.01). C:N ratio ranged between 6 and 8 (Fig. 16C) and were significantly different between areas (ANOVA, F$_{3.27}$ = 6.37; p < 0.001) (Fig. 17C). Higher values were observed in S1 compared to S2, whereas no difference was found between S3 and S4, which had intermediate values compared to S1 and S2 (Tukey HSD, p < 0.05). In general, we observed an increase in C:N ratio with depth, however this trend was only statistically significant in the area 2 (k = -0.004, p < 0.01) and 3 (k= -0.006, p < 0.05).
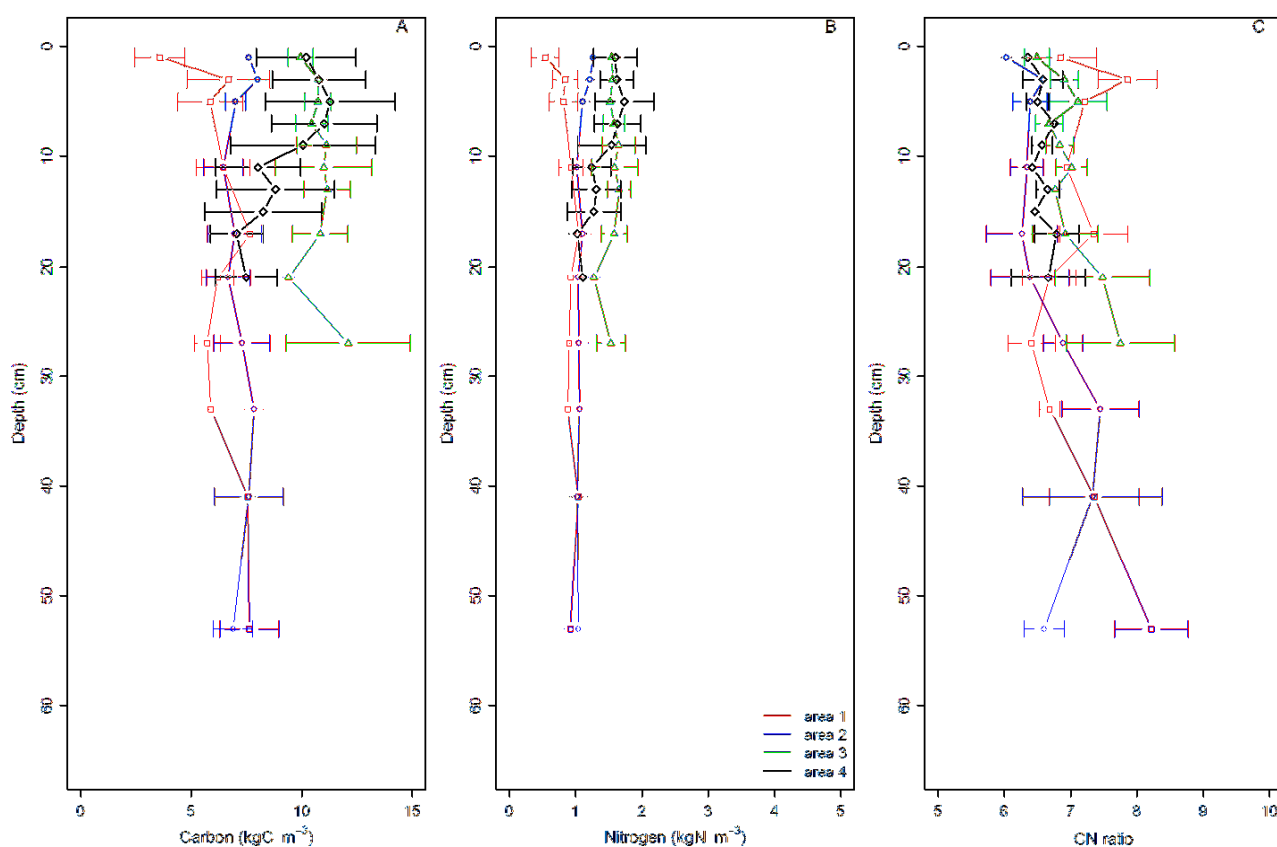

Figure 16. Depth profiles of sediment Carbon (A), Nitrogen (B) and CN ratio (C) in each area. Details as in Fig. 13.
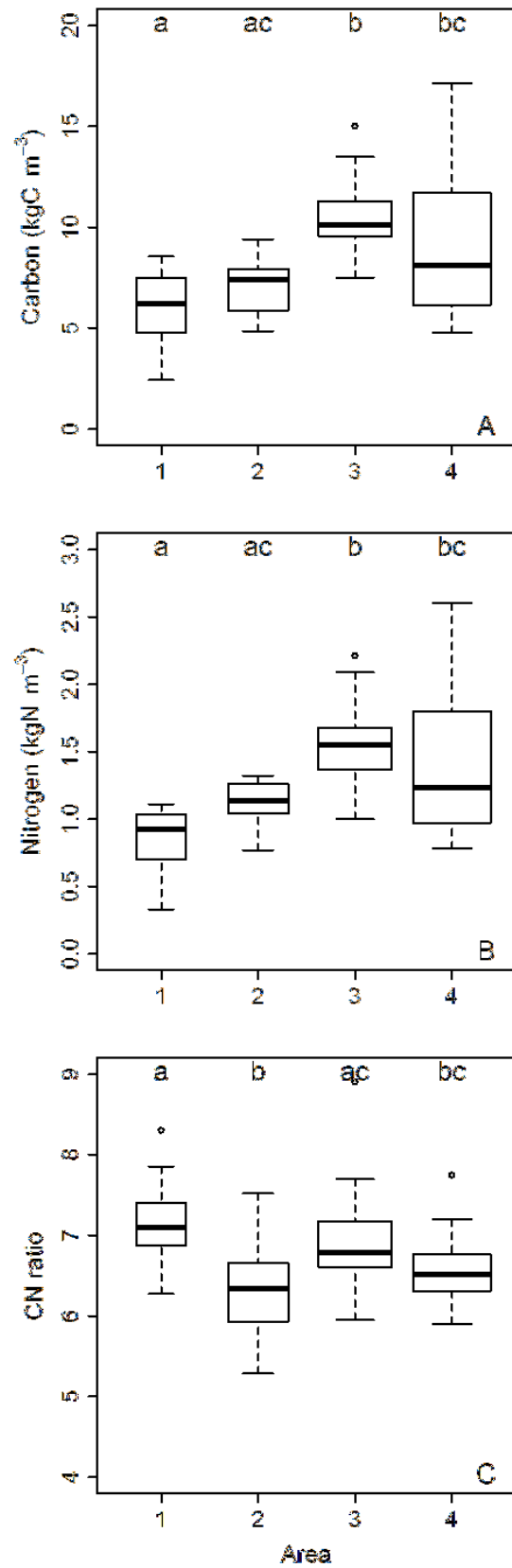
Figure 17. Boxplots of surface (0 -22 cm) sediment Carbon (A), Nitrogen (B) and CN ratio (C) in each area. Details as in Fig. 13.

3.5 $\delta^{13}C$ and $\delta^{15}N$

Carbon stable isotope values ranged between -16 to -26 (Fig. 18A) and were significantly different between areas (ANOVA, $F_{3.27} = 23.61$; $p < 0.01$). S1 and S3 formed one group whereas S2 and S4 formed a lower second group (Fig. 19A, Tukey HSD $p < 0.05$). $\delta^{13}C$ did not change significantly with depth in any of the areas except in area 2 were $\delta^{13}C$ decreased with depth ($k = -0.001$, $p < 0.05$). $\delta^{15}N$ values ranged between 4 and 8 (Fig. 18B) and were significantly different between vegetated areas (S1 and S4) and bare areas (S2 and S3) (Fig 19B, ANOVA, $F_{3.27} = 32.41$; $p < 0.001$, Tukey HSD $p < 0.05$). Profiles showed a decrease with depth, however the changes with depth were only statistically significant for area 3 ($k = 0.009$, $p < 0.01$).
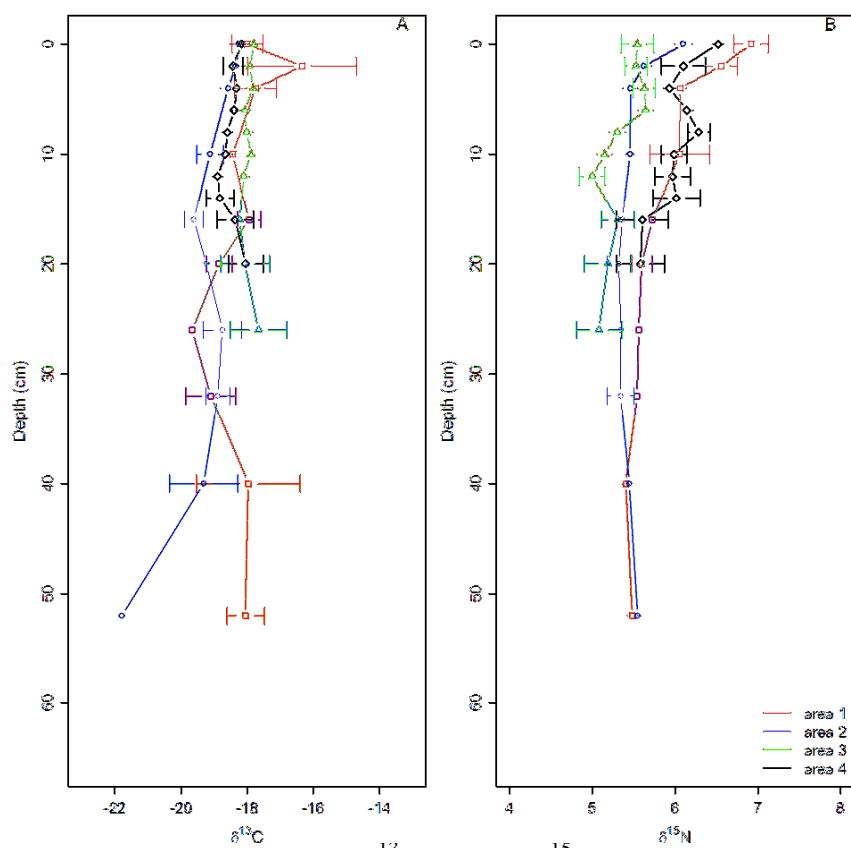

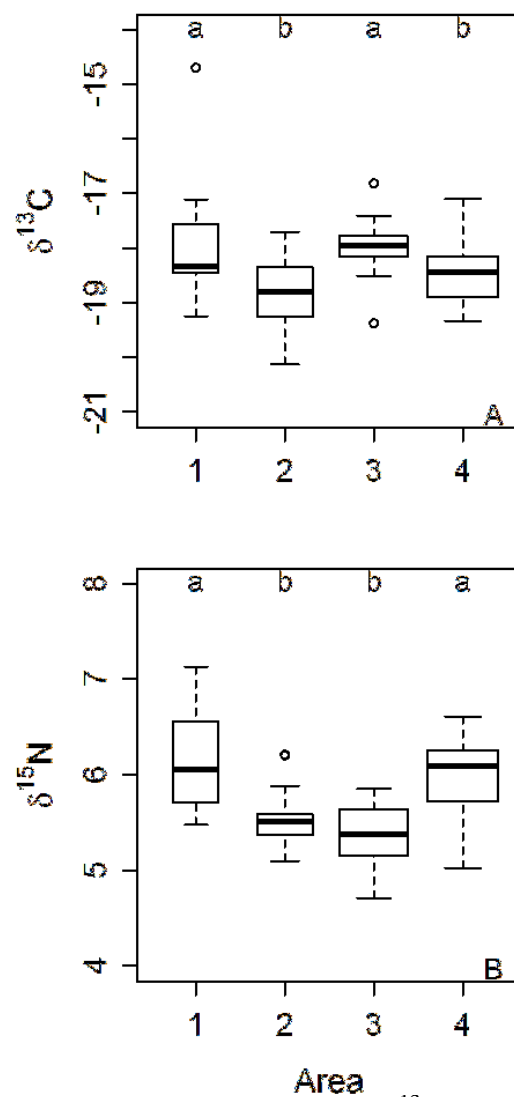Figure 18. Depth profiles of sediment $\delta^{13}C$ (A) and $\delta^{15}N$ (B) in each area. Details as in Fig. 13.

Figure 19. Boxplots of surface (0 -22 cm) sediment $\delta^{13}C$ (A) and $\delta^{15}N$ (B) in each area. Details as in Fig. 13.

DISCUSSION

4.1 Differences between areas and depth profiles

The experimental design involved analysing key biogeochemical properties, like plant biomass aboveground and belowground, contents of organic matter, C and N, and isotopic fractionation of C and N contents of the sediment along a four points transect in the Trocadero Island saltmarshes, from a *Zoostera noltii* dominated bed (S1) in the low saltmarsh to a *Spartina maritima* dominated sediment in the high saltmarsh (S4). This transect represent a sea to land gradient in marine influence. The intermediate sampling stations in this transect from sea to land were bare sediment (S2) and an area of bare sediment with disperse *Spartina maritima* plants (S3). These four habitats are characteristic of the Cadiz Bay Natural Park and of many other temperate saltmarshes (Davis jr. et al., 2004; PORN, Bahía de Cadiz).

The biomass of *Zoostera nolti* and *Spartina maritima* in the area 1 and 4 was similar both above ground and below ground (Fig. 11). The underground biomass of both communities was concentrated in the upper 18 cm, showing a decreasing trend with depth in both communities (Fig. 12). Despite this coincidences in biomass and distribution of the below ground biomass, the impact of both types of plant communities in the biogeochemical characteristics of the sediment might be very different for a number of reasons. There might exist differences in production between both communities, both below ground and above ground (Ibañez et al., 1999, 2000, Valiela et al., 2000, Sousa et al., 2010) and also they are likely to affect in different ways the hydrodynamics and therefore the capacity of the bed to capture and retain particles (Peralta et al. 2008). In addition, as a source of detritus the biomass of *Z. nolti* and *S. maritima* differs in their C and N stoichiometric composition. *Z nolti* presented a lower C:N ratio than *S. maritima*, being from 6 to 28 and from 14 to 33, respectively. Therefore, the detritus from *S. maritima* is more refractory to microbial degradation than that of *Z nolti*, since it is well known that the biodegradability of plant detritus is directly related to its N content (Rice et al., 1981, Enriquez et al 1993). The difference in biodegradability affects the persistence of the detritus within a given system and increases its probability of being exported to adjacent habitats as well.

The bare sediment area (S2) was deprived of macrophytes, being a so-called unvegetated sediment at the time of sampling. This zone is typically inhabited by a microphytobenthic community usually dominated by benthic diatoms (Corzo et al. 2009, Garcia-Robledo et al. 2010). However this area is seasonally colonized by blooms of the green macroalgae *Ulva* sp, that in the Bay of Cádiz occupy this area in winter (Corzo et al. 2010). The area S3 is similar to area S2 but with scattered *S. maritima* plants. It is positioned at a higher height in the tidal range which means that the emersion period is larger than in area S2.

The height in the tidal range of the four sampling areas and therefore their relative position in the sea to land gradient seems to be the most important factor responsible for the differences in the biogeochemical properties of the sediment. In this study, we have found very clear differences in the carbonates contents of the sediment between the areas S1 and S2, the *Z. noltii* bed and the bare sediment, and areas S3 and S4, both inhabited by S. maritima with different degree of cover (Fig. 15). This is likely due to the biogenic precipitation of carbonates in the shell of marine animals that are buried after sedimentation (Schulz et al., 2006). The organic matter content in the upper 22 cm of the sediment was highly different between replicates collected from the same area, suggesting a high heterogeneity in the sediment. Likely due to this high heterogeneity the differences among areas were not significant (Fig. 14). However, the content in C and N in the upper 22 cm of the sediment in the areas 3 and 4 were significantly higher than C and N contents in the areas 1(Fig. 17). The C:N ratios in the upper 22 cm layer of the sediment was the lowest in the area 2 (Fig. 17). This is consisting with this area being inhabited by microalgae and therefore with a relatively low C:N ratio (Meyers, 1994). The highest C:N ratios were found in the area 1 inhabited by *Z. noltii*. It is surprising the little differences in the C:N ratios among areas despite the larger differences in the C:N ratio of the plant community colonising each area that might act as potential source of detritus. The mean C:N ratio of the sediment at the Trocadero Island saltmarshes in all areas was between 6 and 8. This low C:N ratio in the sediment suggest that either most of organic matter present in the sediment was derived from a source with a low C:N ratio like phytoplankton or microphyobenthos (Garcia et al., 2002) or that the microalgae and bacterial biomass was high enough as to increase considerably the N content of the sediment (Craft et al., 1988).

The pattern of differences in $\delta^{13}C$ values appeared to be relatively similar to the CN ratios; values in S2 were lower than S1, suggesting a foreign influence for one of those sites. The bare area is broadly colonized by algae, like *Ulva spp.* with low $\delta^{13}C$ values (Corzo et al. 2010), microphytobenthos and diatomes (Corzo et al. 2009, Garcia-Robledo et al. 2010).

However, values in S3 and S4 were also similar to S1. Those similitudes are related to the vegetation cover.

S2 was also the only area where a trend of decreasing $\delta^{13}C$ values with depth was found. It was also similar in S1 and it is caused by the carbonates approaching from sea (Schulz et al., 2006) that increase the carbon content on sediment.

Whilst $\delta^{13}C$ values are strong indicator of the photosynthetic mechanism of potential organic matter sources, $\delta^{15}N$ values generally do not change much between primary producers if the N source is the same. On the other hand microbial processes (such as N fixation and denitrification) can strongly affect sediment $\delta^{15}N$ values (Rice et al., 1981; Enriquez et al., 1993). Within Cadiz Bay $\delta^{15}N$ values of suspended particulate matter (SPM) from N point sources (7 - 9) and macrophytes (3-8) tend to be relatively high, suggesting the influence of N from urban and aquaculture effluent (Morris et al. 2009). Thus, significantly higher $\delta^{15}N$ values in both of the vegetated habitats may represent an important urban effluent (Morris et al. 2009) or the microbiology of the sediment (Craft et al., 1988).

A significant trend of higher $\delta^{15}N$ values in the surface sediments (also coinciding with an increase in N content) was found at S3.

The study of how the different biogeochemical properties analysed in this work changes with depth is complicated by the fact that the length of the cores was not similar for all the sampling areas. It was not possible to collect long cores (> 50 cm) in the area 3 and 4 due to the unexpected abundance of animal borrows (*Uca tangerii*) below 20 cm. However, cores from area 1 and 2 were longer than 50 cm.

The organic matter content of the sediment, when expressed per unit of volume of sediment, tended to increase with depth in all areas (Fig. 13), however this increase with depth was statistically significant only in the areas 1 and 2, but not in areas 3 and 4. This is

likely due to high horizontal heterogeneity observed in all the areas and to fact that cores 3 and 4 were shorter that cores from the areas 1 and 2. This might have contributed to obscure the changes of organic matter with depth in the area 3 and 4. The values measured in this study are slightly higher than those measured at other sites of Cadiz Bay (Establier et al 1984). The increasing trend in organic matter with depth could be explained by a general decrease in the input of organic matter to the sediment due to a decrease in primary production in the recent years or by changes in the preservation rate of this detritus within the sediment. Similarly the organic carbon content showed no significant trend with depth at all sites (Fig.16). However, N profiles, visually, showed a decreasing trend with depth but changes were only significant for site S3 (Fig.16). The C:N ratio tended to increase with depth but changes were only significant for sites S2 and S3. The absence of clear trends with depth for OM, C, N and C:N ratio might be due to several factors. The high horizontal heterogeneity existing in all sites difficult the appreciation of a clear pattern with depth. All vertical profiles presented a number of "peaks and valleys" that could be due to seasonal or interannual variability. In addition, resuspension events, bioturbation and reworking of the sediment surface due to very intense "marisqueo" could mixed the sediment avoiding the formation of clear trends with depth. Flat vertical profiles of OM, C, N and C:N have been observed in previous studies in the Cadiz Bay and in other saltmarshes (Establier et al. 1984, Gebrehiwet et al. 2008). Carbonate content increased significantly with depth for sites S1 and S2 but not site S3 and S4, probably because the cores were shorter for these two sites (Fig.15). Carbonate content in the Cadiz bay is of biogenic origin (Muñoz & Sanchez Lamadrid 1994). The increase with depth could be due to a lower sedimentation of this biogenic material in recent years which might be connected with a general decrease of productivity in Cadiz Bay as suggested above to explain the increase of OM with depth. The balance between dissolution and precipitation of carbonate mediated by the biological activity might play a role in the observed trend (Corzo et al. 2005).

4.2 Possible sources of organic matter

To help with the identification of potential organic matter sources to intertidal sediments within the study area, biplots of $\delta^{13}C$ against CN ratios and $\delta^{15}N$ values of the sediments and plant tissues collected nearby to the cores are presented (Fig. 20 and 21). S1,

S2, S3 and S4 have more or less the same values of $\delta^{13}C$ and $\delta^{15}N$. It means that our samples have more or less the same sources. The $\delta^{13}C$ and $\delta^{15}N$ content of Spartina maritima and Algae are closer to the content of the areas than Zostera noltii. It means that our samples are more affected by those materials. However, Zostera noltii is not far away from the rest (fig. 20).

The graph that show C:Nratio against $\delta^{13}C$ shows that *Z. noltii* may affect more than *S. maritima* the sampling site but algae values are closer to the rest (fig 21).
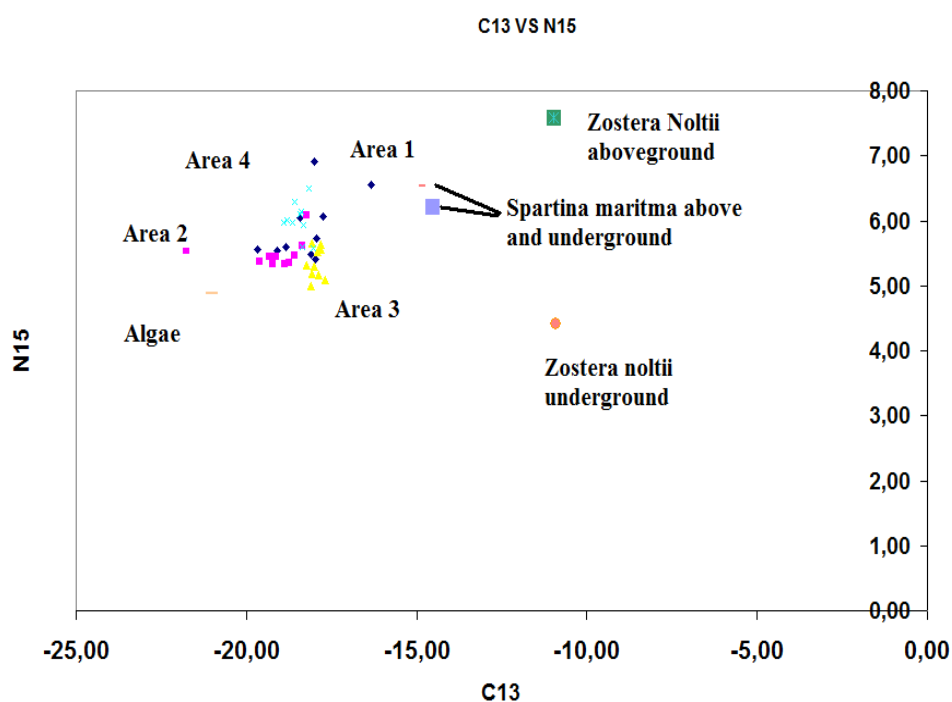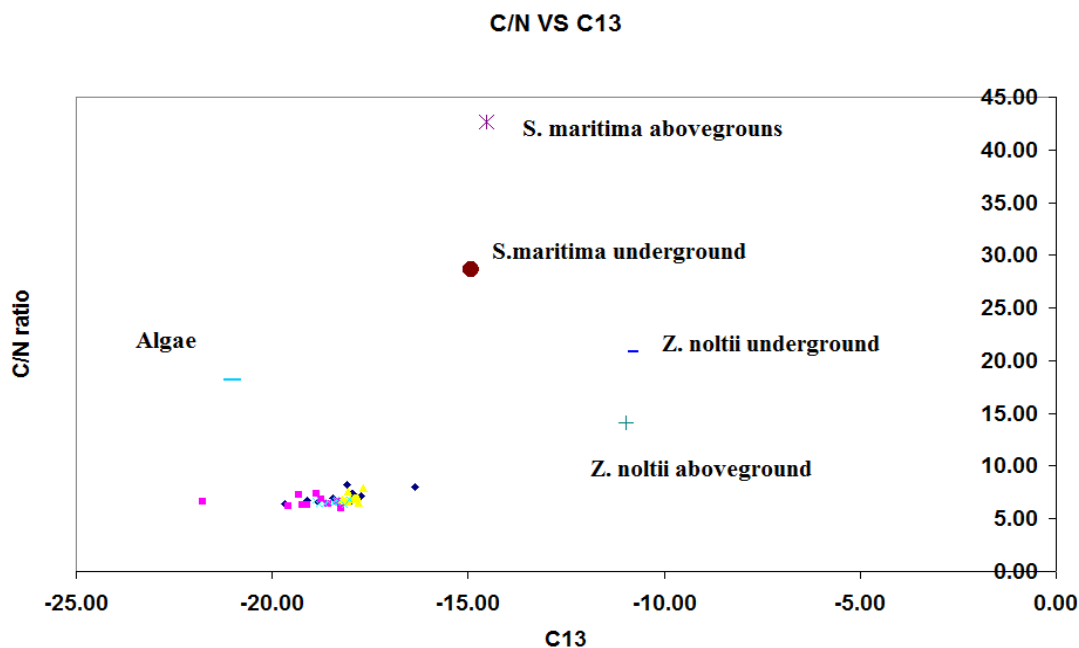

Fig 20: Plot of δ15N against δ13C for our sampling values.

Fig 21: Plot of C/N ratio against δ13C values for our samples.

To help identify sources at the level of the whole bay, we combined the data collected in this study with a database of C and N contents and isotope values maintained in EDEA (data provided by numerous projects, see acknowledgements). Most of the possible sources (invertebrates, epiphytes, seagrasses, macroalgae, SPM, *S. maritima, Salicornia sp*., and sediment from south of the bay) have been plotted in a bag plot. Firstly, δ^{13}C has been plotted against δ^{15}N and the other graph shows the relationship between δ^{13}C and C:N ratio. Those graph showed that all the possible sources appear more or less at the same part of the plot but *Salicornia sp* (The most terrestrial plant) was separated from the rest (fig: 22).

The δ15N content does not vary a lot because the organic matter of those sites has the same sources (fig 22). The SPM is formed by all the bay compounds as it is shown above. *S. maritima* is different from the rest sea plants because it has C4 photosynthetic pathway and the way to capture the C is slightly different. *Salicornia sp*. is a terrestrial plant with C3 photosynthetic pathway and has more depletion of δ13C. The macroalgae affects the composition of the suspended particulate matter (SPM). The sediments from our sampling site are mainly affected by macroalgae and SPM.

The C:N ratio has been plotted against δ^{13}C (fig 22 B). The macroalgae affect the SPM. The *S. maritima* has been separated from the rest vegetation because of its

photosynthetic pathway. The sediments from North (our study site) and south have different depletion of δ^{13}C. It could be because in the south there are more epiphytes than in our study area and at this the terrestrial affection is greater. However, the sampled sediment is mainly affected by SPM and macroalgae as we deduced above.
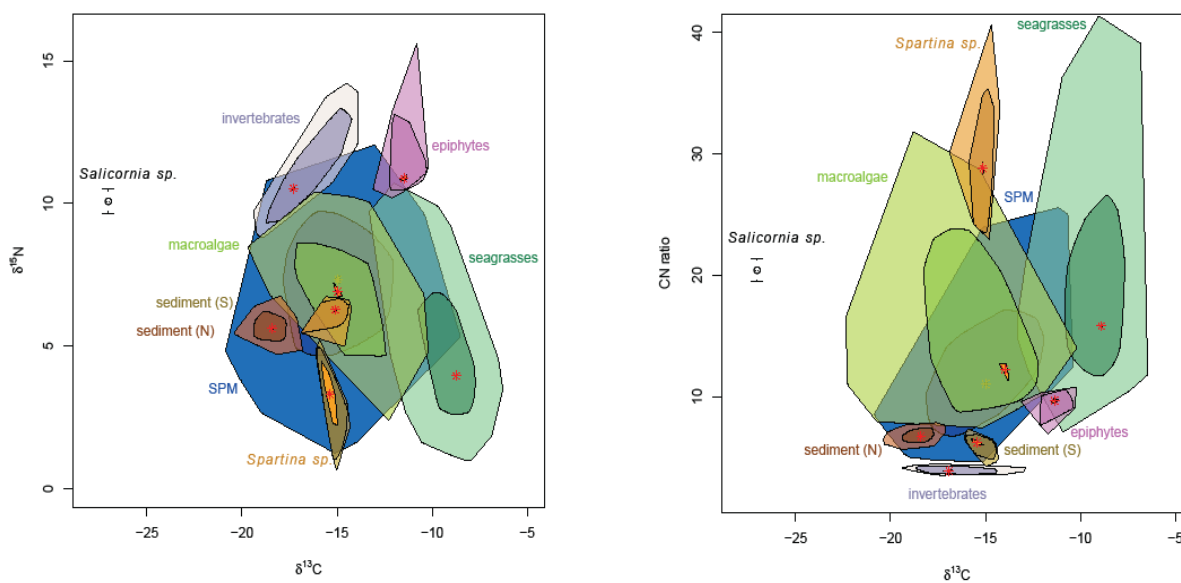

Fig 22: Values of δ15N against δ13C (right side) and C:N ratio against δ13C (left side) for values from EDEA database.

4.3 Estimation of long-term OM burial rates

Using equation 1, long-term OM burial rates (g m^{-2} y^{-1}) can be estimated from measurements of sediment OM concentration, C_i (kg m^{-3}) multiplied by a suitable estimation of sediment accretion rates, ω (m y^{-1}) (Middelburg et al. 2004). In this study (an intertidal transect on Trocadero island, N. Cadiz Inner Bay), no significant differences in OM concentration were found between areas or with depth, thus to calculate burial rates the mean value for all areas was used (68 kg m^{-3}). For organic C and N, the mean value of S1 and S2 (*Z. noltii*, 6.9 kg C m^{-3}, 1.0 kg N m^{-3}) and the mean of S3 and S4 (*S. maritima*, 10.0 kg C m^{-3}, 1.5 kg N m^{-3}) were used in calculations. These values were comparable to previous extensive studies of sediment OM content for the whole of Cadiz Inner Bay (Establier et al., 1984). Thus, to upscale burial estimates to the whole bay we used the mean

of this study combined with the previously published values (assuming a dry bulk density of 0.75 g-sed cm^{-3}; OM = 23.4 kg m^{-3}, 12.4 kg C m^{-3}, 1.4 kg N m^{-3})

The long-term sediment accretion rates for 3 points in the inner bay were previously published by Ligero et al., (2002); ranging from 0.16 to 0.27 cm y^{-1} in the south and north of the bay, respectively. These estimates were made by dating cores collected in sub-tidal areas (and the type of surface vegetation was not mentioned), thus they probably underestimate saltmarsh accretion rates. Still, the highest value was derived relatively close to the study transect, thus we used this value of 0.27 cm y^{-1} to upscale estimates from this study. At the scale of the bay, we use the range in accretion rates to provide the first, tentative estimate of OM burial for the bay.

The burial rate for organic matter in our study site is estimated as 184 g OM m^{-2} y^{-1}. For the *Z. noltii* habitat organic nutrient burial is estimated as 18.6 g C m^{-2} y^{-1} and 2.7 g N m^{-2} y^{-1}, and in the saltmarsh as 27 g C m^{-2} y^{-1} and 4.1 g N m^{-2} y^{-1}. At the scale of the bay areal burial rates are estimated to be between 73 – 123 g OM m^{-2} y^{-1}, which represents organic C and N burial rates of between 15.6 – 26.4 g C m^{-2} y^{-1}, and 2.1 – 3.5 g N m^{-2}y^{-1}, respectively. Thus, total annual C and N burial rates for the inner bay, which has an area of 30 km^2 (of which the intertidal area is about 13 km^2), are estimated to be about 630 t-C y^{-1} and 84 t-N y^{-1}.
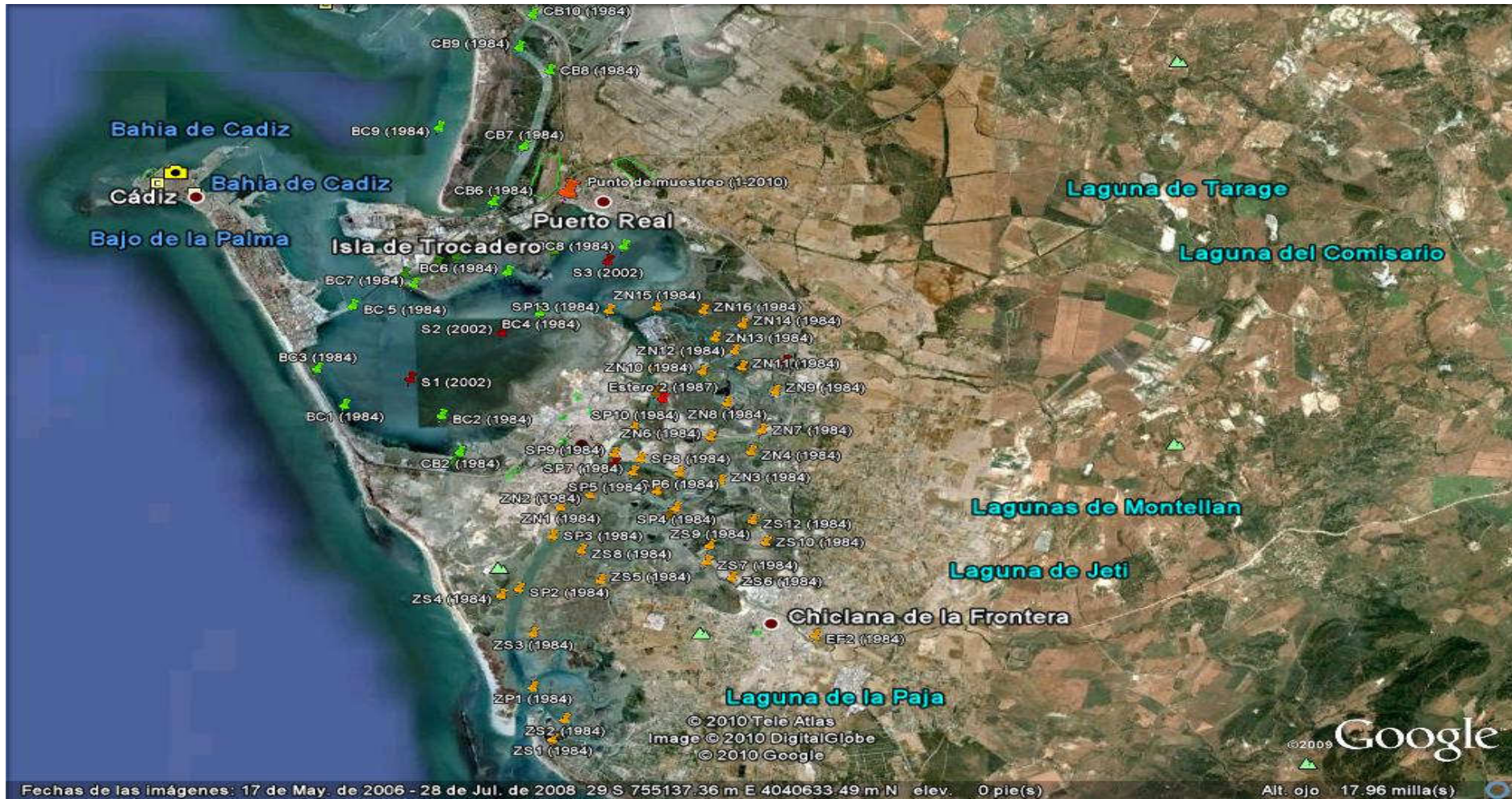
Fig 23: Points used to calculate the burial rate. The red inside the bay were used for sedimentation rate (Ligero et al., 2002) and the rest to calculate organic matter, nitrogen and carbon content of sediment (Establier et al., 1984).

CONCLUSION

The biogeochemical properties of sediments from the different habitats were affected by their position in the sea to land gradient and therefore their characteristic tidal height. Carbonate concentrations increased toward the sea (the *Z. noltii* habitat), and organic C and N tended to increase toward the land (the saltmarsh). Horizontal heterogeneity was high within each area, which probably hindered the observation of clear differences between habitats and changes of the biogeochemical properties with depth. The vertical profiles presented a number of "peaks and valleys" that may be due to inter-annual variability in benthic OM fluxes. On the other hand, the absence of clear trends with depth for most biogeochemical properties might be a consequence of a very intense mixing due to resuspension, bioturbation and reworking of surface sediments shell fishing activities.

Organic matter sources were similar between the areas, suggesting mixing of the multiple inputs. Sediments did not have similar CN ratios and δ^{13}C values to the macrophytes suggesting that a substantial fraction of accreted OM is derived from micoalgae (phytoplankton and microphytobenthos) and possibly macroalgae. Substantial transformation and recycling of macrophyte tissues may also help explain this result. More studies with different biomarkers may help to further confirm the magnitude of these different sources.

C burial rates in the vegetated habitats were relatively close to the mean estimate for coastal shelf sediments (20 g C m^{-2} y^{-1}), lower than the average for estuaries (50 g C m^{-2} y^{-1}) and much below the average for vegetated habitats (120 g C m^{-2} $^{y-1}$) (Nellemann et al., 2010). Suggesting, vegetated habitats in Cadiz Bay may not function as such strong C sinks as would have been predicted. On the other hand, estimations of long-term accretion rates in each habitat may possibly increase this estimate (or at least give a more definite answer). Although, large changes in organic C were not observed with depth, if the below-ground biomass of the vegetated areas is considered, there appears to be a substantial "loss" of C and N from the sediments, which may represent high mineralisation rates.

Overall, C and N burial within the Inner bay is estimated to be substantial, 630 t C y^{-1} and 84 t N y^{-1}, which for example, is more than the amount of C and N contained within

the dominant macrophyte beds, *C. prolifera* during spring-summer (524 t C and 45 t N, Morris et al. 2009) and much more than contained in the maximum bloom of green algae in winter (31 t C and 3.7 t N, Camarena-Gomez, M. T., pers. com.).

Acknowledgements

LITERATURE

Adam P., 1990. *Saltmarsh Ecology*, Cambridge University Press. New York.

Arthur Chen C., Borges A.V., 2009. *Reconciling opposing views on carbon cycling in the coastal ocean: Continental shelves as sink and near-shore ecosystems as sources of atmospheric CO2*. Deep-Sea Research II. 56: 578-590.

Avance de la adaptación-revisión del plan general de ordenación urbanística. Cádiz, 2007.

Balázs H, Opara-Nadib O. and Beesea F., 2004. *A simple method for measuring* 10.2136/2004.0010.

Carrasco, M., López-Ramírez, JA, Benavente, J., López-Aguayo, F. and Sales, D. 2003. *Assessment of urban and industrial contamination levels in the Bay of Cádiz, SW Spain.* Marine Pollution Bulletin*, **46:*** 335–345

Cebrián J, 2002. *Variability and control of carbon consumption, export and accumulation in marine communities*. Limnol Oceanogr 47:11–22

Cheng-Tung, A.C., Borges A.V., 2009. *Reconciling opposing views on carbon cyclingin the coastal ocean: continental shelves as sinks and near-shore ecosystems as sources of atmospheric CO^2*. Deep Sea Research II. Vol. 56, 578-590.

Corzo, A., Luzon, A., Mayayo, M. J., van Bergeijk, S. A., Mata, P., García de Lomas, J. (2005) *Carbonate mineralogy along a biogeochemical gradient in recent lacustrine sediments of Gallocanta Lake (Spain).* Geomicrob. J. 22: 283-298.

Costanza R., d'Arge R., Groot R., Farber S., Grasso M., Hannon B., Limburg K., Naeem S., O'Neill R.V., Paruelo J., Raskin R.G., Sutton P., vanden Belt M.; 1987. *The Value of the World's Ecosystem Services and Natural Capital.* Nature, 387: 253-260. USA.

Craft, C.B., Broome, S.W., Senece, E.D., Showers, W.J., 1988. *Estimating sources of soil organic matter in natural and transplanting salt marshes using stable isotopes of carbon and nitrogen. Estuarine,* Coastal and shelf science. Vol. 26, 633-641.

Duarte, C. M. and J. Cebrian. 1996. *The Fate of Marine Autotrophic Production*. Limnology and Oceanography, Vol. 41, No. 8. Pp 1758-1766.

Edwards K.R., Mills K.P., 2005. *Aboveground and belowground productivity of Spartina alterniflora (smooth cord-grass) in natural and created Louisiana salt marsh stuaries*. 28, 252-265.

Environmental knowledge for change, Blue Carbon. 2009. <http://www.grida.no/publications/rr/blue-carbon/ > (20 de marzo de 2010)

Enriquez,S., Duarte C.M., Sand-Jenssen, 1993. *Patterns in decomposition rates among photosinthetic organisms: The importance of detritus C:N:P content*. Oecologia.

Establier, R., Blasco, J., Gómez, A., Escolar. D., 1984. *Materia orgánica en los sedimentos de la bahía de Cádiz y sus zonas de marisma y salinas*. Investigación pesquera. Vol. 48 (2), 285-301.

Hendriks, I. E., Bouma, T. J., Morris, E. P. & Duarte, C. M., 2010. *Effects of seagrasses and algae of the Caulerpa family on hydrodynamics and particle-trapping rates.* Marine Biology 157, 473-481. IF-ISI-2008: 1.953.

Ibañez C., Day Jr., Pont, D., 1999. *Primary production and decomposition of wetlands of the Rhone Delta, France: interactive impacts of human modifications and relative sea level rise.* Journal of Coastal research 15, 717-731.

Ibañez C., Curcó A., Day Jr. J.W., Prat N., 2000. *Structure and productivity of microtidal mediterranean coastal marshes.* In: Weinstein, M.P., Kreeger, D.A. (Eds), Concepts and controversies in tidal marsh ecology. Kuwer Academic Publishers. Netherlands. Pp. 107-136.

Ligero R.A., Barrera M., Casas Ruiz, M, Sales D., López-Aguayo F.; 2002. *Dating of marine sediments and time evolution of heavy metal concentration in the Cadiz bay, Spain.* Environmental pollution. Vol. 118, 97-108.

Lillebo, A. I., Neto J.M., Flindt M.R., Marquez J.C., and Pardal M.A.. 2004. *Phosphorous dynamics in a temperate intertidal estuary*. Estuar. Coast. Shelf Sci. 61: 101–109.

Machas R., Santos, R., Peterson B., 2003. *Tracing the flow of organic matter from primary producers to filter feeders in Ria Formosa lagoon, Southern Portugal*. Estuaries. Vol 26, 846-856.

McGathery K.J., Sundback K., Anderson IC2007. *Eutrophication in shallow coastal bays and lagoons: The role of plants in the coastal filter.* Marine Ecology Progress Series.

Meyers, P.A., Ishiwatari, R., 1994. *Lacustrine organic geochemistryman overview of indicators of organic matter sources and diagenesis in lake sediments. Organic geochemistry*. Vol 20, 867-900.

Middelburg, J.J., Soetaert, K., Herman, P.M.J., Boschker, H.T.S. and Heip, C.H.R. (2004) *Burial of nutrients in coastal sediments: The role of primary producers*. In, Nielsen S.L., Banta G.T., Pedersen M.F. (eds.) "Estuarine nutrient cycling: the influence of primary producers: the fate of nutrients and biomass*". Kluwer, Dordrecht. pp: 217-230

Morris E.P., Peralta G., Brun F.G, Van Duren L., Bouma T.J., Perez-Llorens J.L., 2008. *Interaction between hydrodynamics and seagrass canopy structure: Spatially explicit effects on ammonium uptake rates.* Limnology and Oceanography. Vol 53: 1531-1539.

Muñoz J.L. y Sánchez de Lamadrid R. A. ,1994. *El medio físico y biológico en la Bahía de Cádiz: Saco Interior.* Informaciones Técnicas 28/29. Consejería de Agricultura y Pesca. Junta de Andalucía.

Nielsen SL, Banta GT, Pedersen MF (2004) *Estuarine nutrient cycling: the influence of primary producers: the fate of nutrients and biomass*. Kluwer, Dordrecht. 303 p.

Niencheski L.F.H.; Windom H.L.; Moore W.S.; Jahnke R.A.; 2007. *Submarine groundwater discharge of nutrients to the ocean along a coastal lagoon barrier,Southern Brazil*. Marine Chemistry, 106: 546-561. Rio Grande do Sul.

Paneque P.; Rodriguez V.; Ojeda S.; 2007. *Lectura geográfica de la bahía de Cadiz: singularidades y conflictos.*

Peralta G., Van Duren L., Morris E., Bouma T., 2008. *Consequences of shoot density and stiffness for ecosistema engineering by benthic macrophytes in flow dominated areas: a hydrodynamic flume study*. Marine Ecology Progress. Series 368103-115.

PORN, Bahía de Cádiz.

Raven JA , Walker DI, Johnston AM, Handley LL, Kübler JE. *1995 b . Implications of ^{13} C natural abundance measurements for photosynthetic performance by marine macrophytes in their natural environment.* Marine Ecology Progress Sciences *123 : 193 –*205.

Schulz, Horst D., Zabel, Matthias, 2006. *Marine Geochemistry.* Springer (ed)

Sousa A.I., Lillebo A., Caçador I., Pardal, M.A., 2008. *Contribution of Spartina maritima to the reduction of eutrophication in estuarine systems*. Environmental pollution. Vol. 156, 628-635.

Sousa A.I.; Lilleb A.; Pardal M.; Cazador I.; 2010. *Productive and nutrient cycling in salt marshes: contribution to ecosystem health*. In Press, corrected Proof.

Valiela, I., Cole, M.L., Mcclalland, J., Hauxwell, J., Cebrian, J., Joye, S.B., 2000. *Role of marshes as part of coastal landscapes.* In: Weinstein, M.P., Kreeger, D.A. (Eds), Concepts and controversies in tidal marsh ecology. Kuwer Academic Publishers. Netherlands. Pp. 23-38.

Wang and Cai, 2004. *A "Marsh CO 2 Pump" for Transferring Carbon from Air to Sea*. Limnology and oceanography. Vol 49: 341-354.

Whitaker, R.H., 1975. *Comunities and ecosystems*. Mcmillan publishing. New York.

Windom H.; Niencheski F.; 2003. *Biogeochemical processes in freshwater-seawater mixing zone in permeable sediments along the coast of Southern Brazil*. Marine chemistry, 83: 121-130. Rio Grande do Sul.

AGRADECIMIENTOS

Me gustaría agradecer esta tesis a mis padres, sin los cuáles esto no sería posible, darles gracias por haber confiado siempre en mí y por apoyarme en todos mis proyectos. Espero no defraudaros nunca.

Aunque ya he dado las gracias al departamento, agradecer especialmente a Juanlu por toda esa ayuda recibida y por aguantar la mala leche esporádica que me entraba, espero que te vaya todo muy bien. A Carmen, por prestarme su ayuda y dejarme observar datos de su tesis. A Emilio porque siempre me has resuelto dudas cuando te he preguntado. A Alfonso por dejarme colaborar en el departamento, ya que ha sido una bonita experiencia y por su ayuda cuando lo he necesitado. Y como no a Edward, por toda tu ayuda prestada y por estas últimas semanas que entre Tere y yo no te hemos dejado descansar, espero que todo siga muy bien para ti y para todos vosotros. Me alegro mucho e haber tenido toda vuestra ayuda.

Quiero agradecer y pedir disculpas a Almudena, Mónica y José (mis super compañeros de piso) por ayudarme en todo lo que han podido y por tener que aguantar mi mala leche estas últimas semanas, sobretodo tu José (ya sabes, la confianza da asco, jajajaja) al cuál también debo agradecer que en estos últimos días cuando el mundo se me venia abajo, me intentaba levantar conforme podía, de verdad que lo siento. Ahora espero que pasemos bien este tiempo que nos queda viviendo los 3 juntos y estáis de suerte...dejaré de hablaros de mi tesis, jajajaja. También a Tere porque en los momentos más críticos has estado ahí. Como a Celia, por aguantar los ratos de café mientras yo le contaba los problemas que iba teniendo. Lo siento mucho chicos, muchas gracias chicos, sois lo mejor!!

También me gustaría agradecer los ratitos de las comidas a Sara, Paula, Elena, Migue, Carmen, Uxia, Marta, Tere y algunos otros más que habéis aparecido algunos días como Albert, Alejandro,... porque sin esos descansitos no hubiera sido lo mismo.

A Eli por haber compartido conmigo la mufla muy civilizadamente..jejejeje. Y también por tu compañía en el laboratorio.

A Christina y Maria, porque este verano con vosotras en el laboratorio ha sido genial.

Agradecer también a todos mis compañeros de master porque este año ha sido fabuloso y me gustaría volveros a ver a todos.

A toda la gente de Puerto Real: Carlos, Dodo (al cual también agradezco era ayuda en la búsqueda de información inicial de la bahía y de la extracción de cores), Ricardo, Polaco, Heredia; porque sin las escapaditas al cinema de vez en cuando esto no se podría llevar.

Y a todos mis amigos en general, los de la uni, los de mi pueblo... Porque sin tener este buen "background"... uno no podría hacer nada.

Muchas gracias a todos.